

Multi-scale Modeling of Solid State Electrolytes for Next Generation Lithium Batteries

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DOE merit review

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Project ID# bat424

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Overview

Timeline

- Start: 2018
- Finish: 2020
- Completed: 40 %

Budget

- Total project funding
 - DOE share: \$ 900 K
 - Contractor 0
- FY 18: \$ 300 K
- FY 19: \$ 300 K
- FY 20: \$300 K

Barriers

- Barriers addressed
 - Low Conductivity
 - High interfacial impedance
 - Dendrite growth

Partners

- Interactions/ collaborations
 - V. Srinivasan, ANL
 - Z. Chen, ANL
 - B. Narayanan, U of Louisville





Project Objectives and Relevance

- In order to improve the safety of present day lithium ion batteries, replacement of liquid electrolytes with their solid state counterparts is a necessity.
- Multi-scale modelling efforts have been adopted to obtain an *in-depth* understanding of the interaction between the electrode and the solid electrolyte aimed at developing highly efficient solid state electrolytes batteries.
- Properties estimated from DFT calculations feed into the mesoscale models, that analyze overall stability of solid electrolytes against cathodes and anodes.
- Solid state electrolytes with lithium metal anode has the potential to substantially increase the energy density of present day lithium ion batteries.

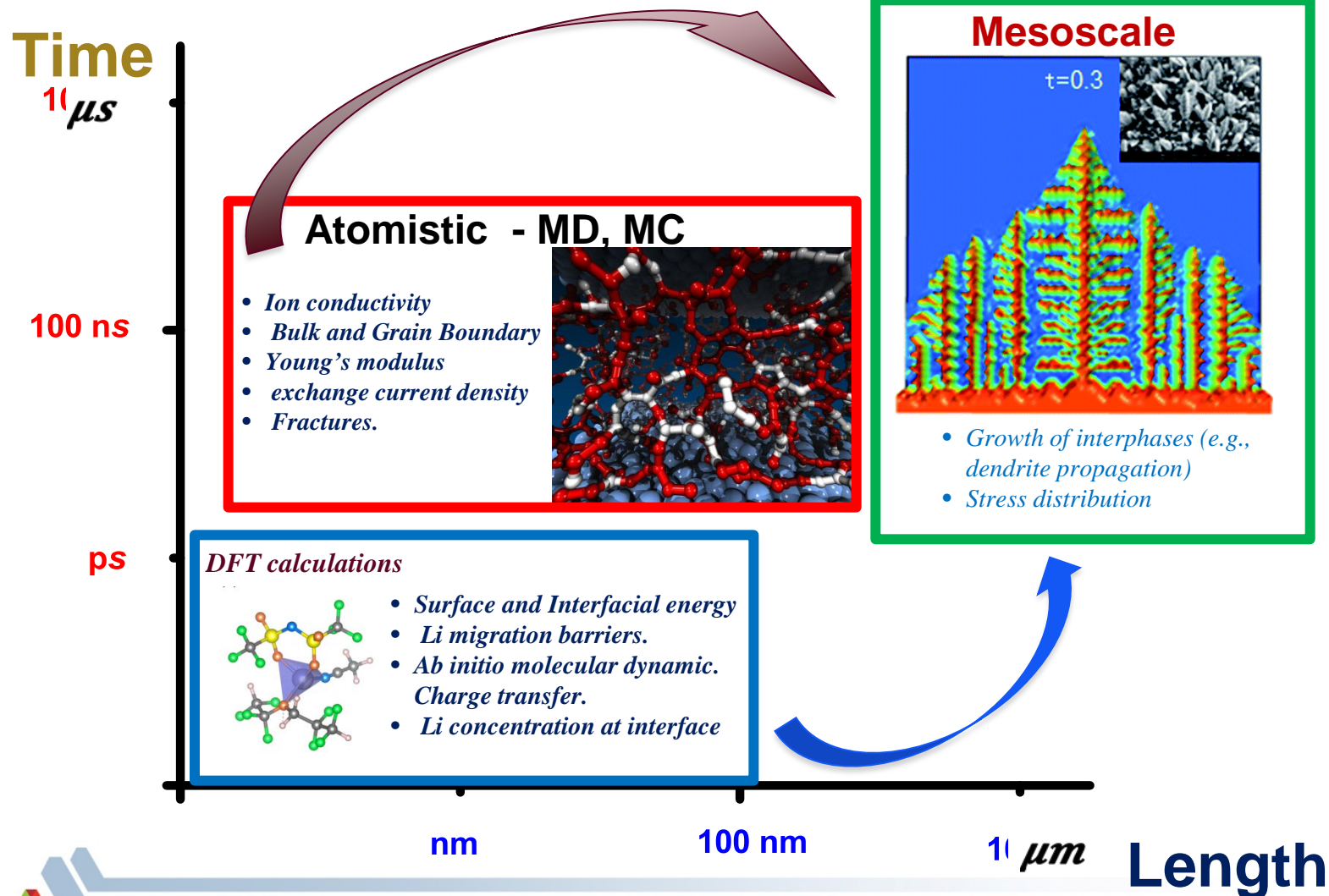
FY19 Milestones

| Month/ Year | Milestones |
|----------------|--|
| Dec/18 | Adoption of LLZO grain and grain-boundary elastic and transport properties and LLZO/Li interfacial properties from DFT to continuum based mesoscale simulations, and comparison with experimental results. Q1 (Completed) |
| Mar/19 | <i>Ab initio</i> molecular dynamics and interfacial formation/binding energy calculations of the interface structure of the LLZO solid electrolyte and NMC 622 cathode material . Q2 (Completed) |
| Jun/19 | Calculations of Li, Ni, Co, Mn migration barriers at interface LLZO/NMC cathode material and estimation of exchange current density between NMC/LLZO. Q3 (Initiated) |
| Sep/19 | Continuum level mesoscale calculations at LLZO/NMC cathode materials. Q4 (Initiated) |



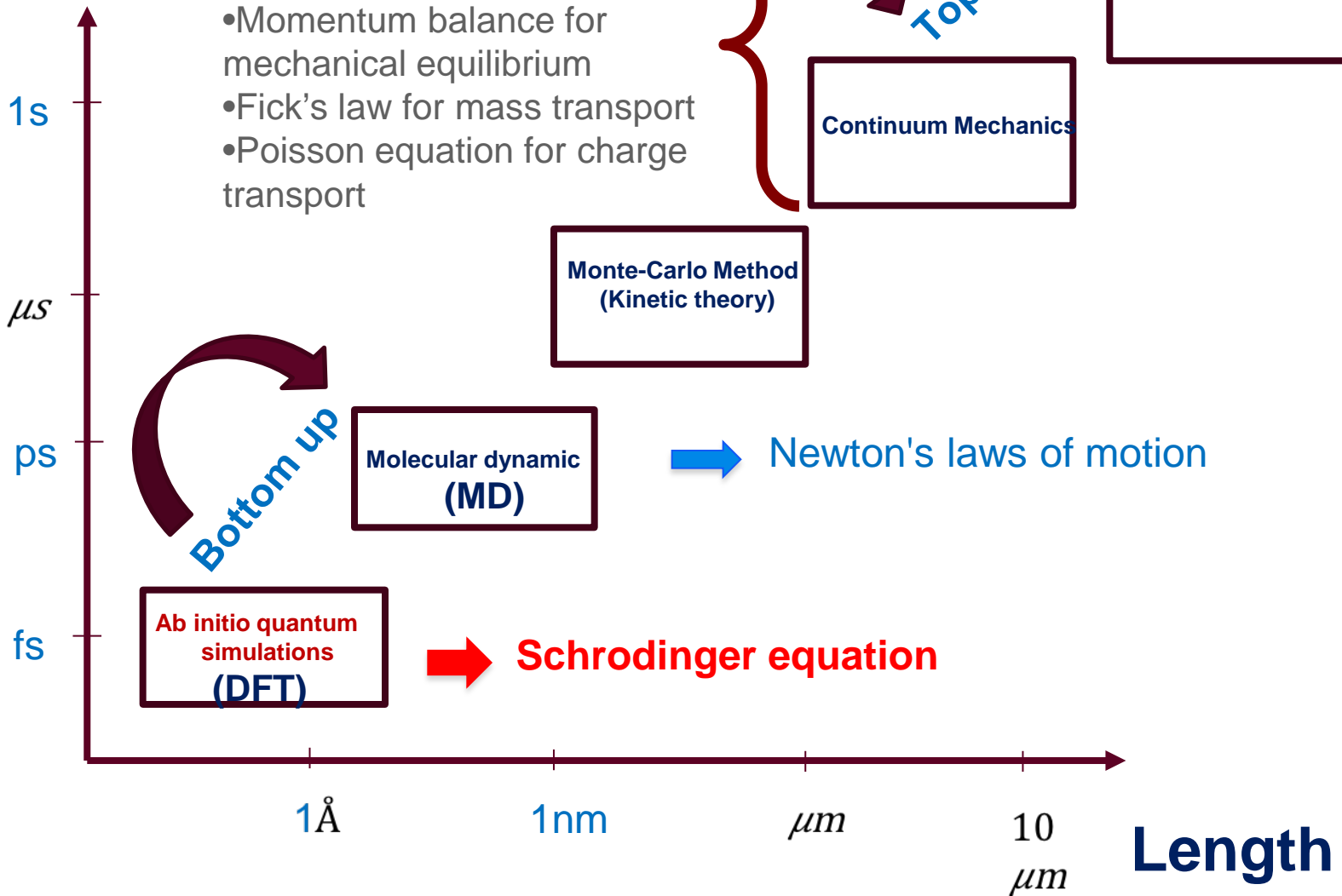
Strategy: A multiscale approach has been adopted, where transport and elastic properties of lithium and solid state electrolytes have been estimated at the nanoscale using DFT calculations, and then the properties have been transferred to the continuum scale model where the mesoscale electrode electrolyte behavior have been analyzed.

Multi-Scale Modeling methods



Computational methods

Time

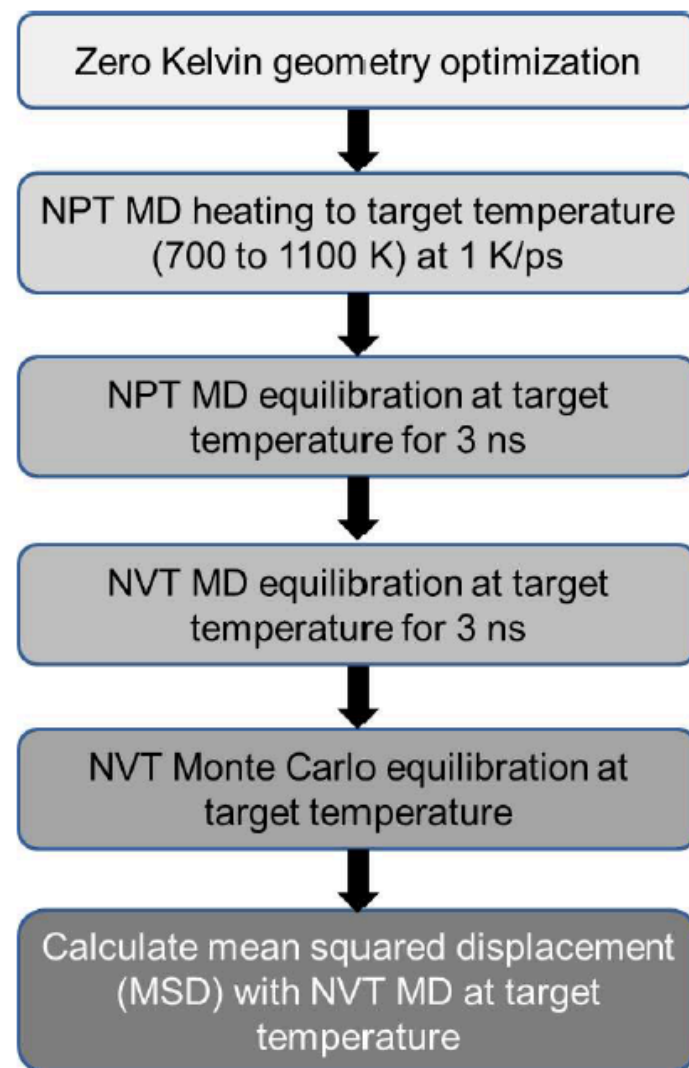


Multi-Scale Modeling in Materials Science



Summary of the computational procedures

- Temperature-based materials simulations.
- Molecular dynamic and Monte-Carlo at operation T.
- **LAMMPS code**
- Elastic and transport properties estimated from the DFT and MD calculations have been imported into the mesoscale simulations, where continuum equations were solved using these parameters to estimate the interfacial stability between solid state electrolyte and anodes and/or cathodes. System ~ 1.9 M atoms
- For mesoscale analysis, all the partial differential equations were solved using a set of codes developed at ANL using MATLAB solver libraries.





Technical Accomplishments

I. Estimation of transport properties in LLZO

- Using DFT, MC and MD simulations, lithium ion conductivity in the bulk and grain-boundary of LLZO has been estimated.
- Exchange current density between the LLZO and Li has also been estimated.

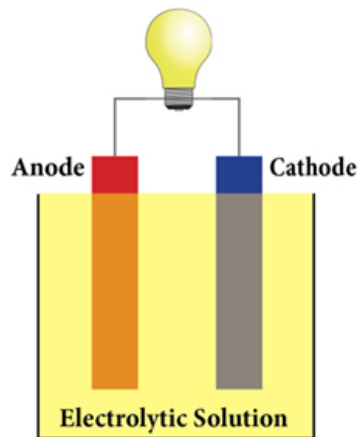
II. Estimation of elastic modulus for LLZO

- Young's modulus in the bulk and grain-boundary of LLZO has been predicted by a combination of MD and DFT techniques.
- Fracture energy of bulk LLZO has also been estimated.

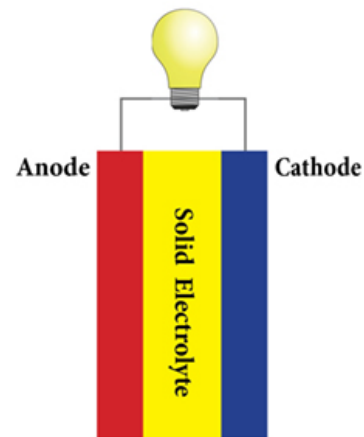
III. Incorporation with mesoscale models

- The transport and elastic properties obtained from the atomistic simulations have been incorporated into the continuum level mesoscale model, where qualitative correlation with experimental results have been obtained regarding critical current density.

Why solid state batteries?



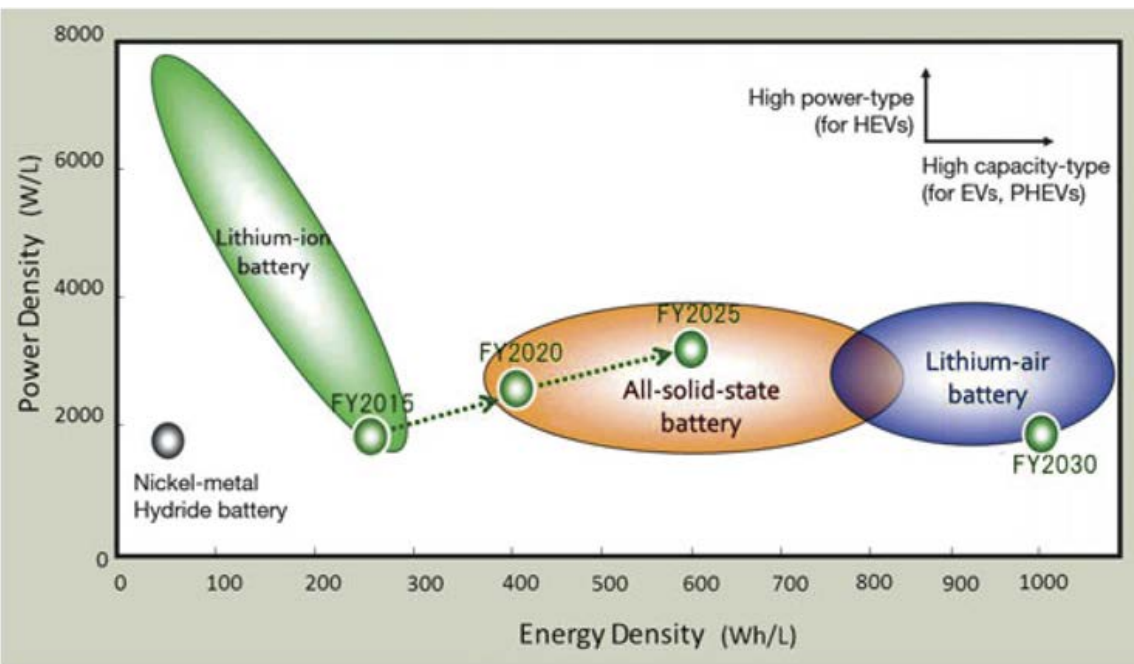
Conventional Battery



All-Solid-State Battery

Potentially:

- Better safety
 - No liquid
 - No flammable solvents
- Easier battery management
 - Bipolar design
 - Small number of cells
- Higher volumetric energy density.



From Toyota



Objectives of solid state electrolyte multi-scale modeling

Overall objectives :

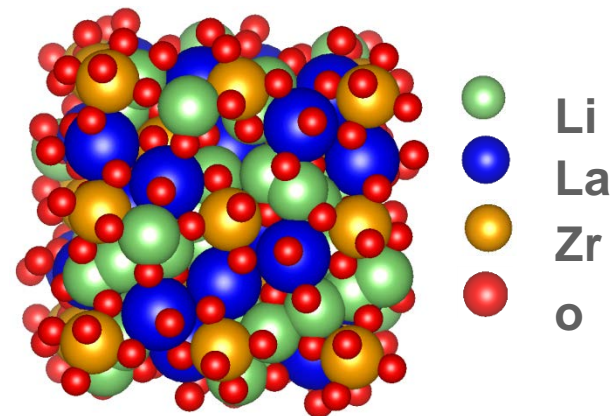
- Develop atomistically-informed microscale models capable of successfully capturing the multi-scale multi-physics phenomena that occurs during Li-metal deposition processes.
- Devise strategies to minimize the impact of degradation mechanisms and enhance the performance and lifetime of next-generation Li-ion batteries.

Atomistic level objectives

- Use atomistic level calculations to obtain parameters needed for accurate mesoscale modeling of grain-interior, grain-boundary, and electrode-electrolyte interfaces
- Investigate degradation mechanisms at the atomistic level to contribute to strategy for minimizing impact on performance

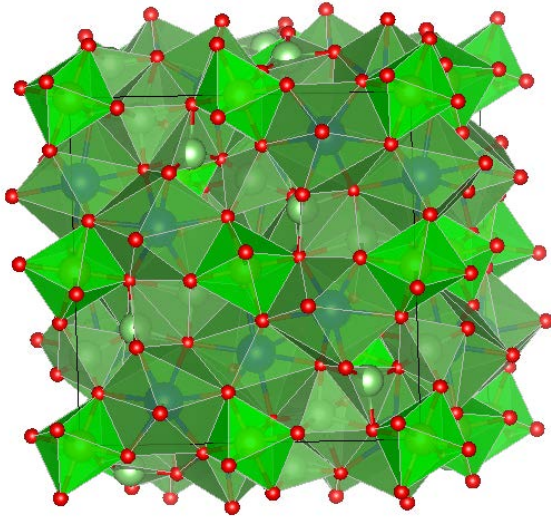
Initial focus:

Electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)



Electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)

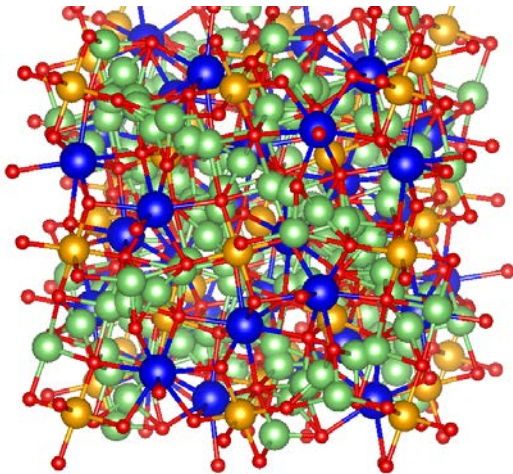
Depending on synthesis temperatures



Tetragonal phase :

$\sigma \sim 10^{-6} \text{ S/cm}$

- Wide working potential, good compatibility with cathode and anode.
- Formation of lithium dendrite along grain boundary, difficult to manufacture, potential stress across the electrode/electrolyte interface
- Anode: mostly Li, although it can be graphite and Si
- Cathode: LiFePO_4 , LiMn_2O_4 , LiCoO_2 , NMC



Cubic phase :

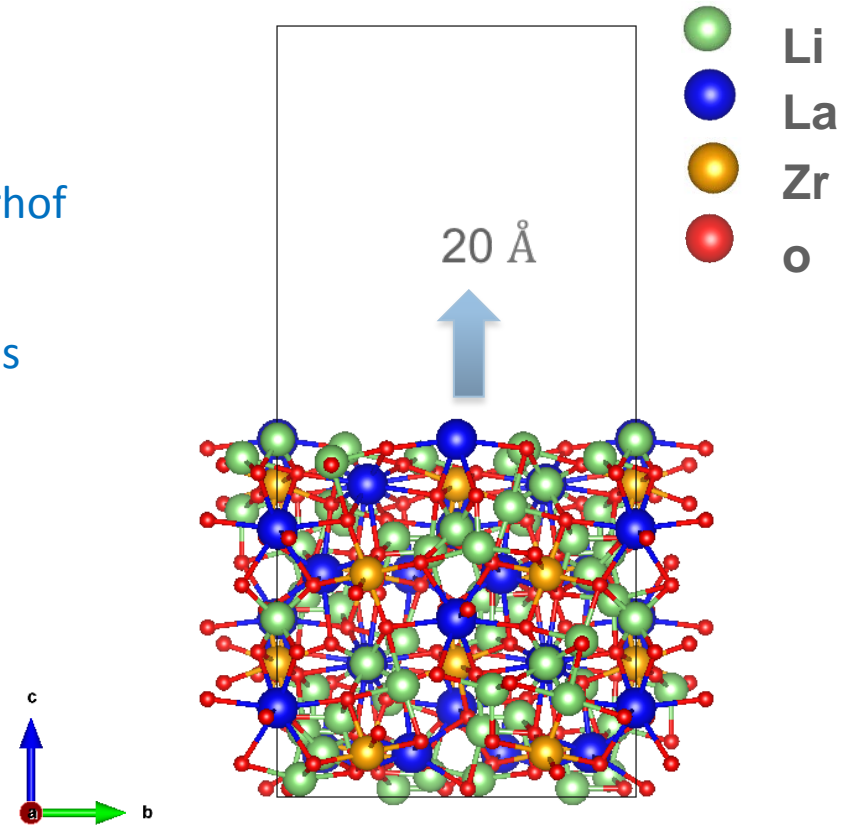
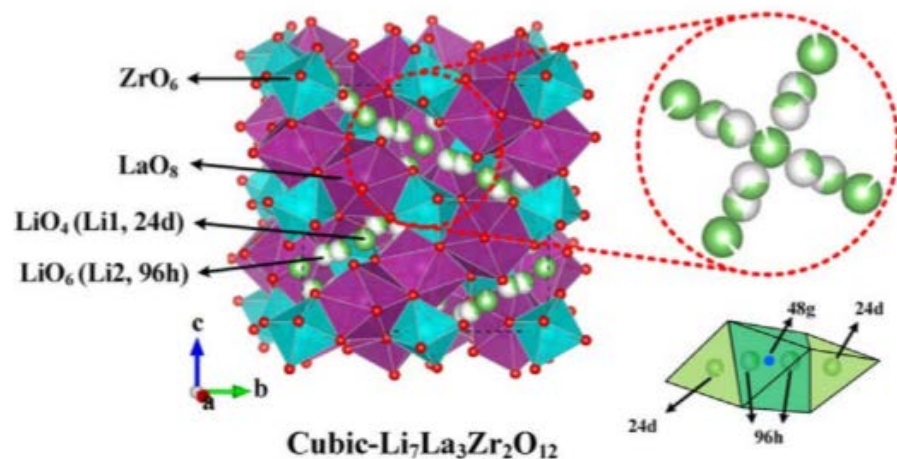
$\sigma \sim 10^{-3} \text{ S/cm}$. $T \sim 25^\circ\text{C}$

K. Kerman et. al. Journal of The Electrochemical Society, 164 (7) A1731-A1744 (2017)

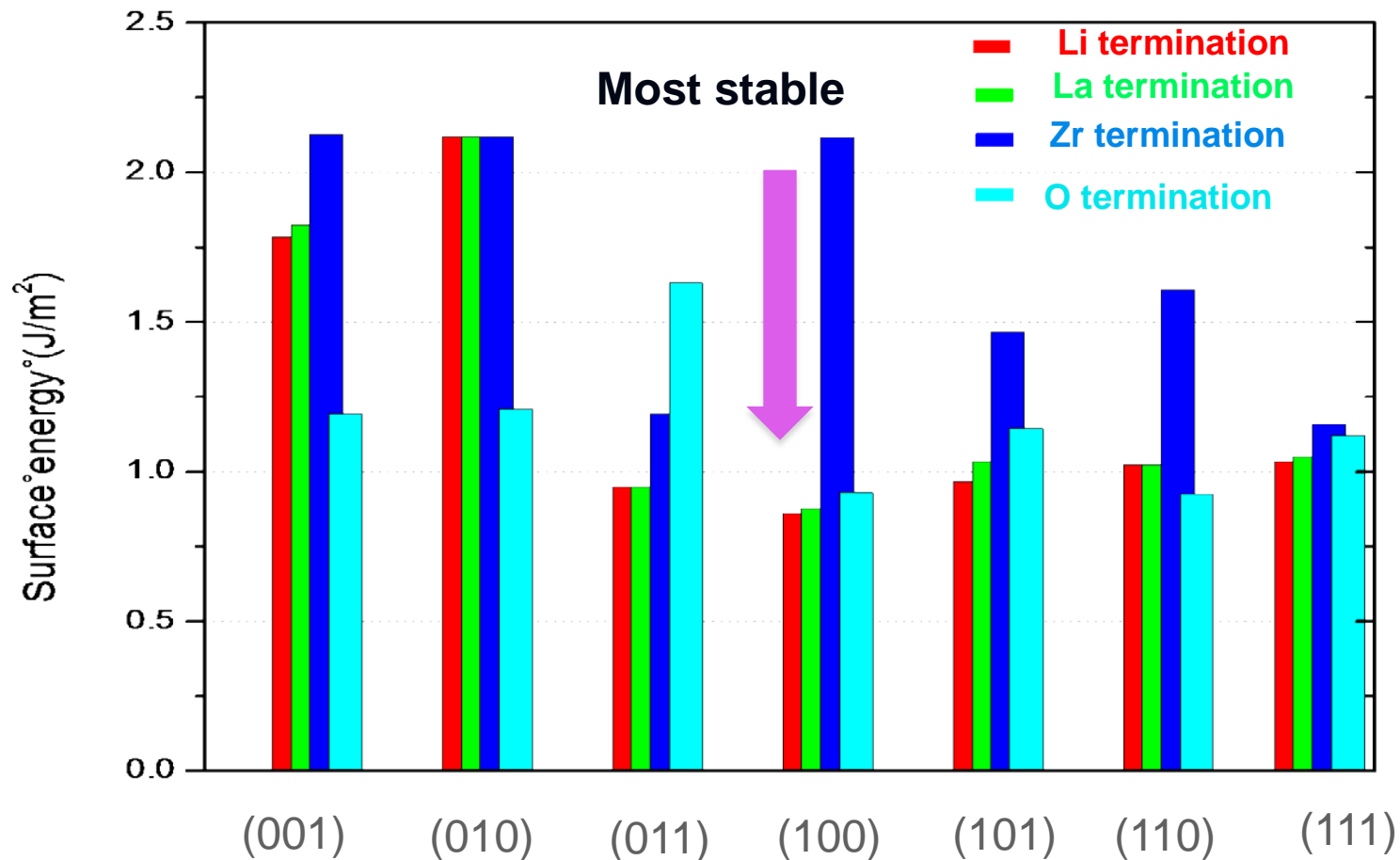
T. Thompson et. al. ACS Energy Lett., 2017, 2 (2), pp 462–468

DFT Analysis: LLZO Surface calculations

- Plane Wave Projector Augmented-Wave (PAW) Density Functional Theory (DFT) methods
- VASP code Spin polarized calculations.
- Generalized Gradient Approximation. Exchange correlation is described by Perdew-Burke-Ernzerhof (PBE) functional.
- 7 surfaces, modeled through stoichiometric slabs with 4 different terminations (28 calculations).
- Supercell : 192 atoms

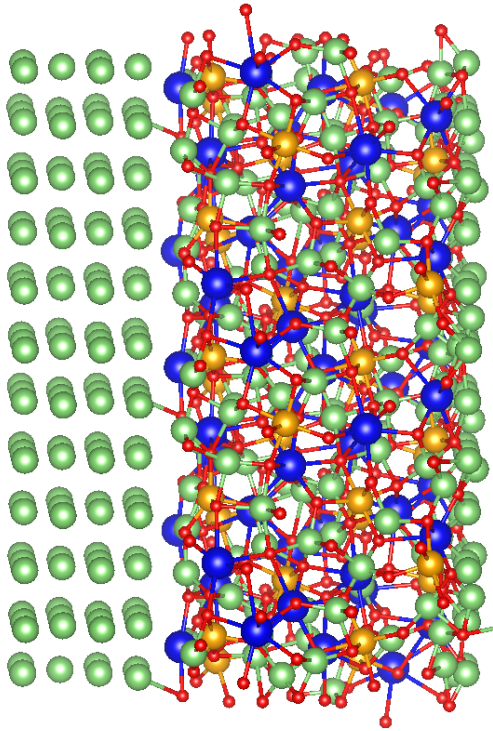


Which LLZO surface is the most stable ?

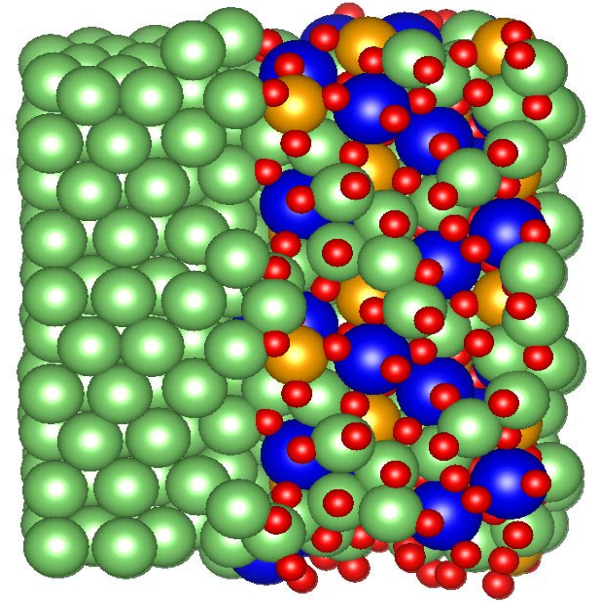


(100) with Li termination gives lowest surface energy; others close in energy

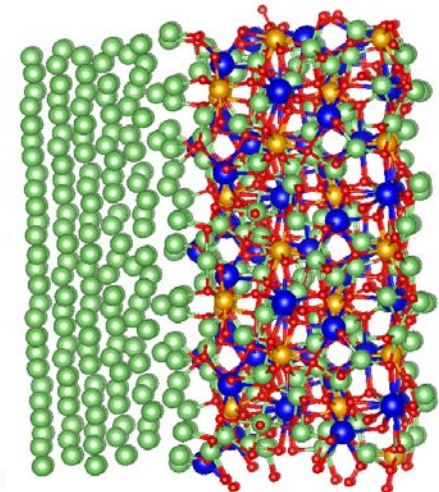
LLZO-Li interfaces



Ab initio MD spin polarized calculations
Using VASP code at T =300k for 20ps



spin polarized DFT



Li (100) /LLZO (100) with Li termination

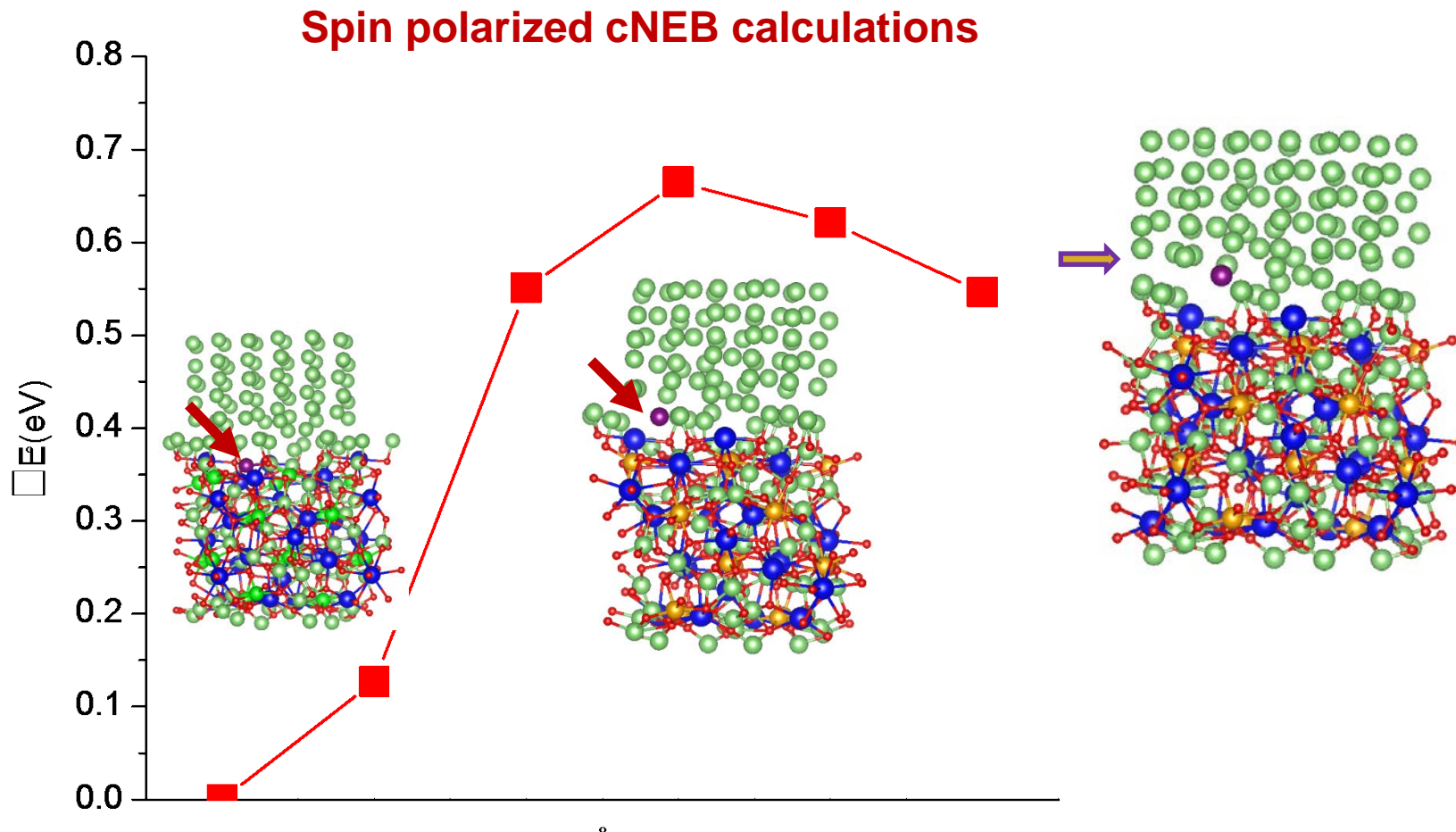
- Exchange current density is defined as:
- Reaction rate constant can be written as:

$$i_0 = Fk_{ref} \cdot (c_{Li^+})^\alpha$$

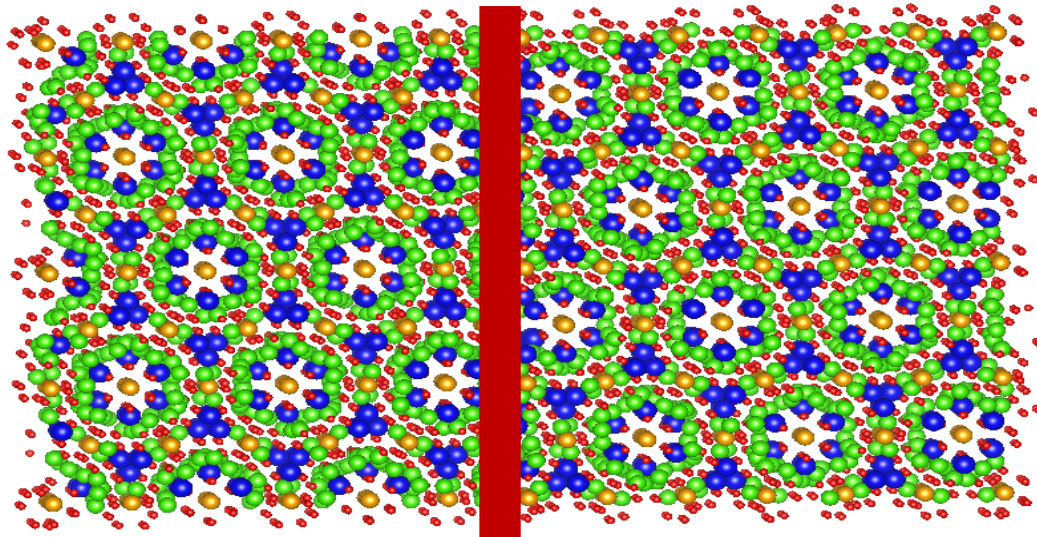
$$k_{ref} = k_0 \exp(-\Delta G/(k_B T))$$



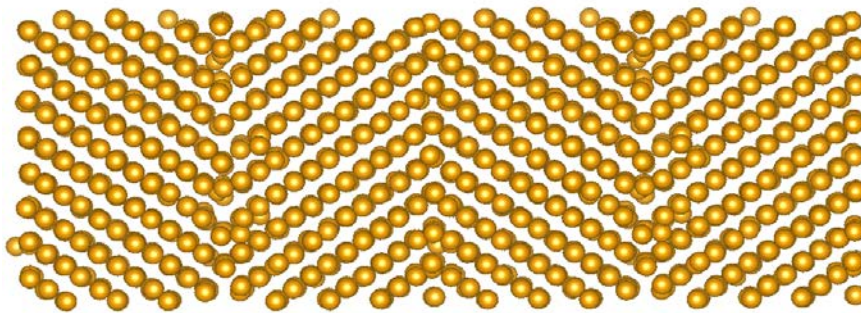
Li (100)/LLZO (100) Interface : Li migration barrier at interface



MD Analysis: LLZO grain boundaries



$\Sigma 5(210)$, All atoms



Only Zr atoms

Properties input for continuum modeling studies:

- barriers for lithium migration at the interface.
- Li ion concentration at GB
- *exchange current density*
- ionic conductivity
- Young's modulus
- Fractures

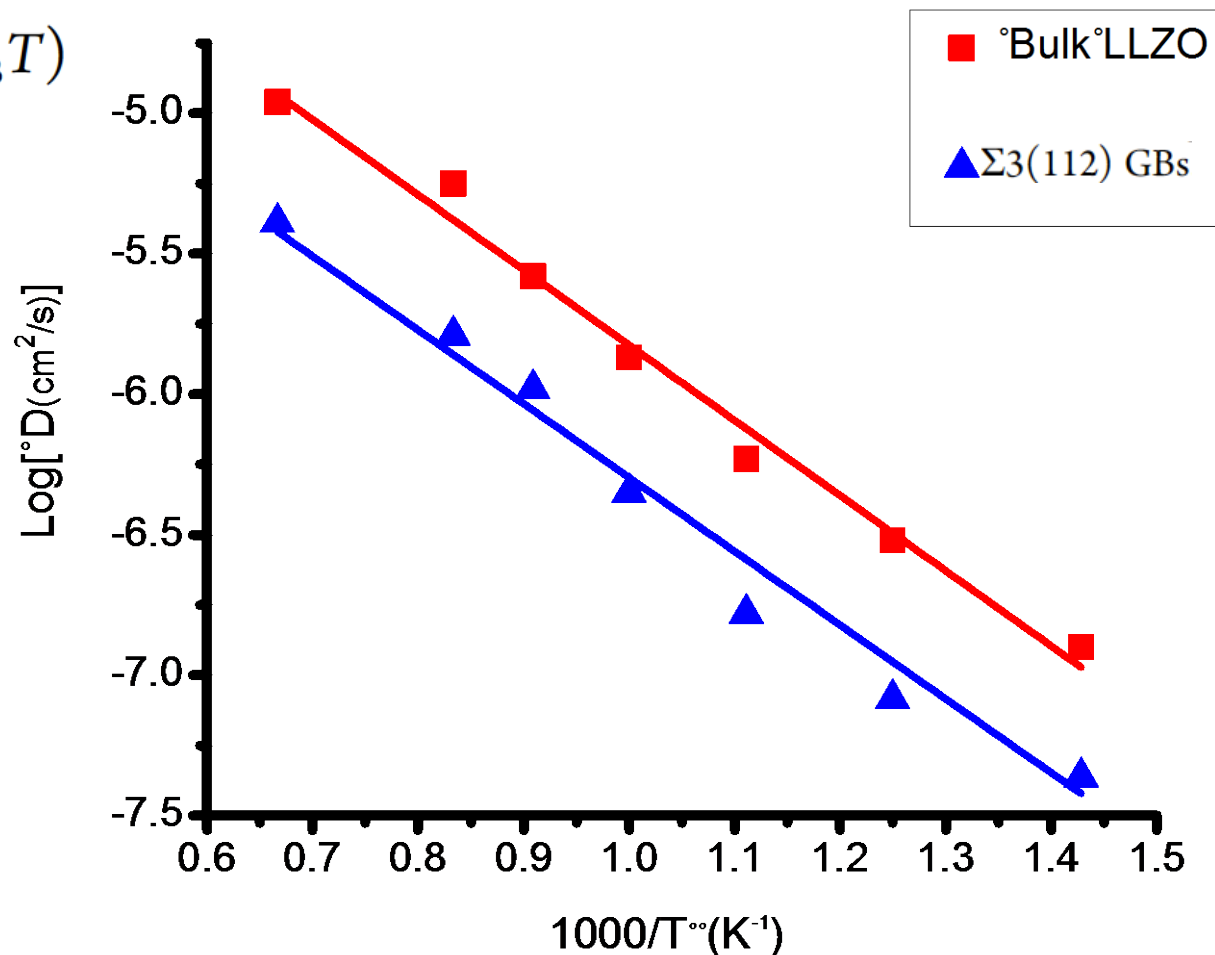
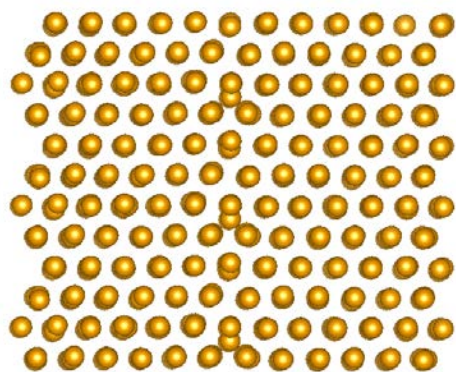
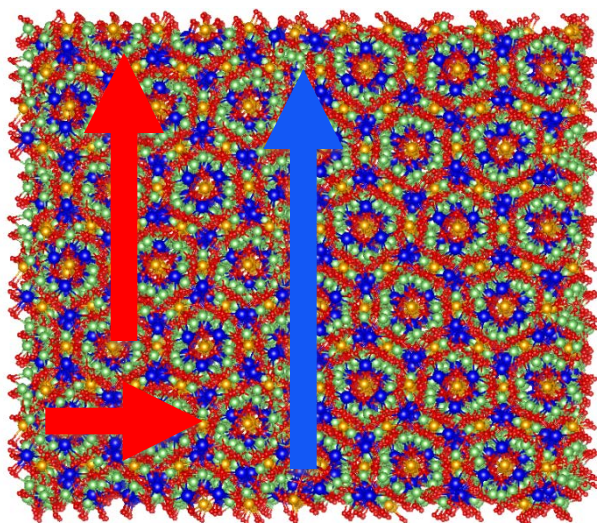




Calculated Li-ion diffusivity D for GB and Bulk

$\Sigma 3(112)$ GBs

$$D(T) = D_0 \exp(-E_a/k_B T)$$

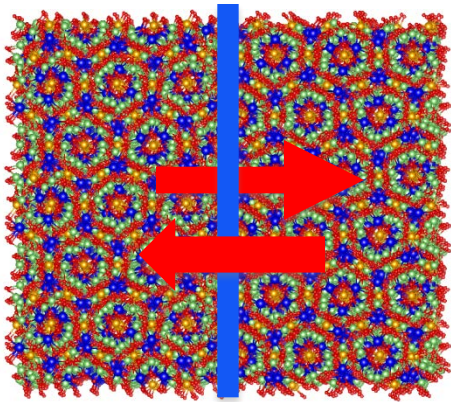


- Ionic conductivity for solid state electrolytes (LLZO) :

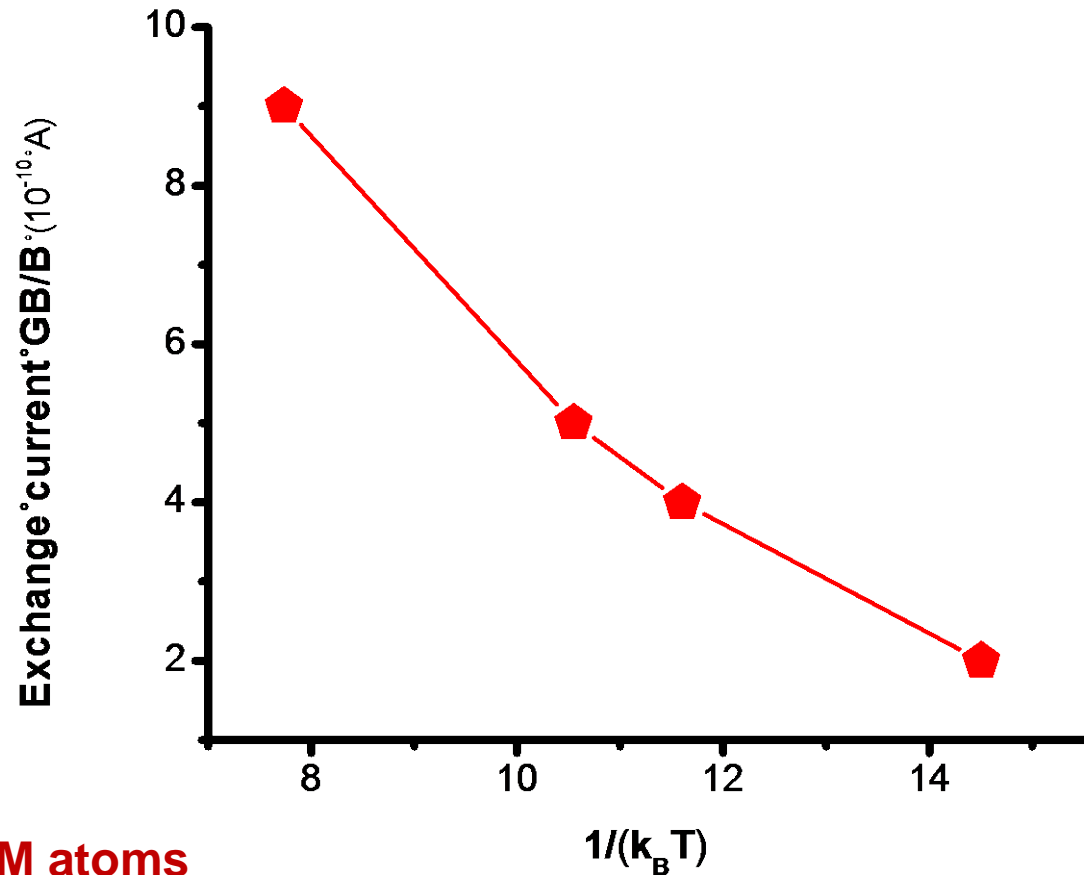
$$\kappa = \frac{F^2}{RT} \cdot D_+ c_+$$



Exchange current between GB and B

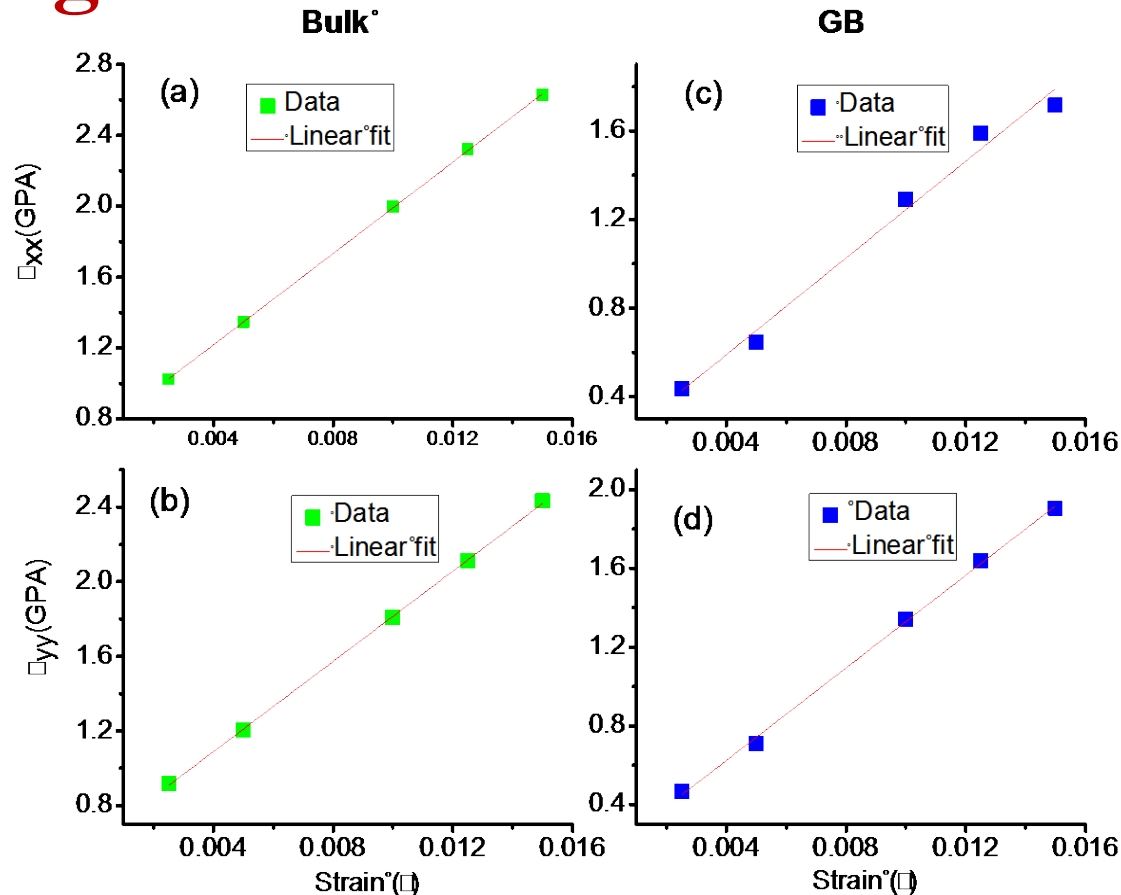


$$I = \Delta Q / \Delta t = (n_+ - n_-) / \Delta t$$



Each T we consider : $\sim 1.9 \text{ M atoms}$

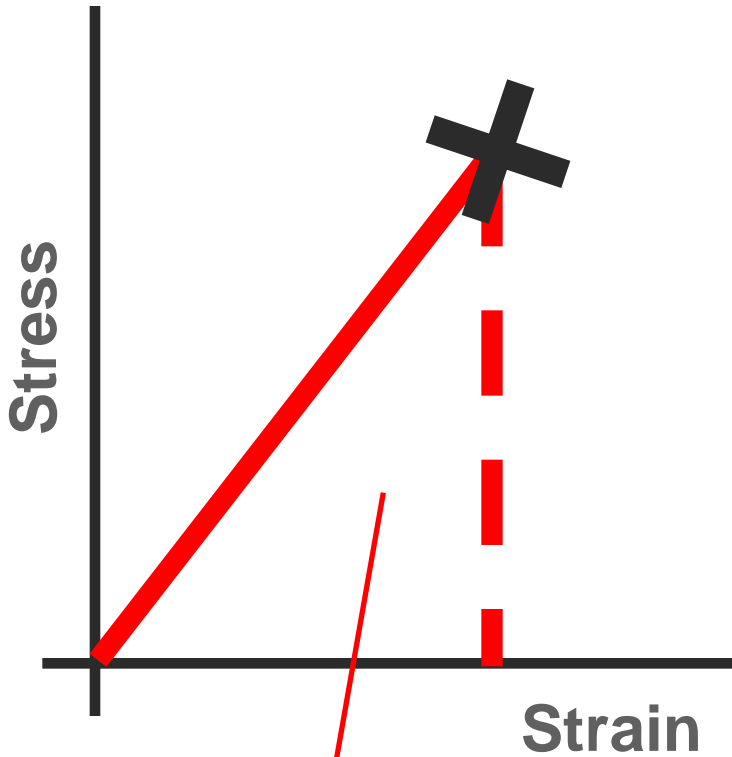
Young's Modulus



The x, y components of the Young's Modulus obtained from our model. (a) and (b) are for the bulk region while (c) and (d) are for GB regions of the $\Sigma_3(112)$ grain boundary.

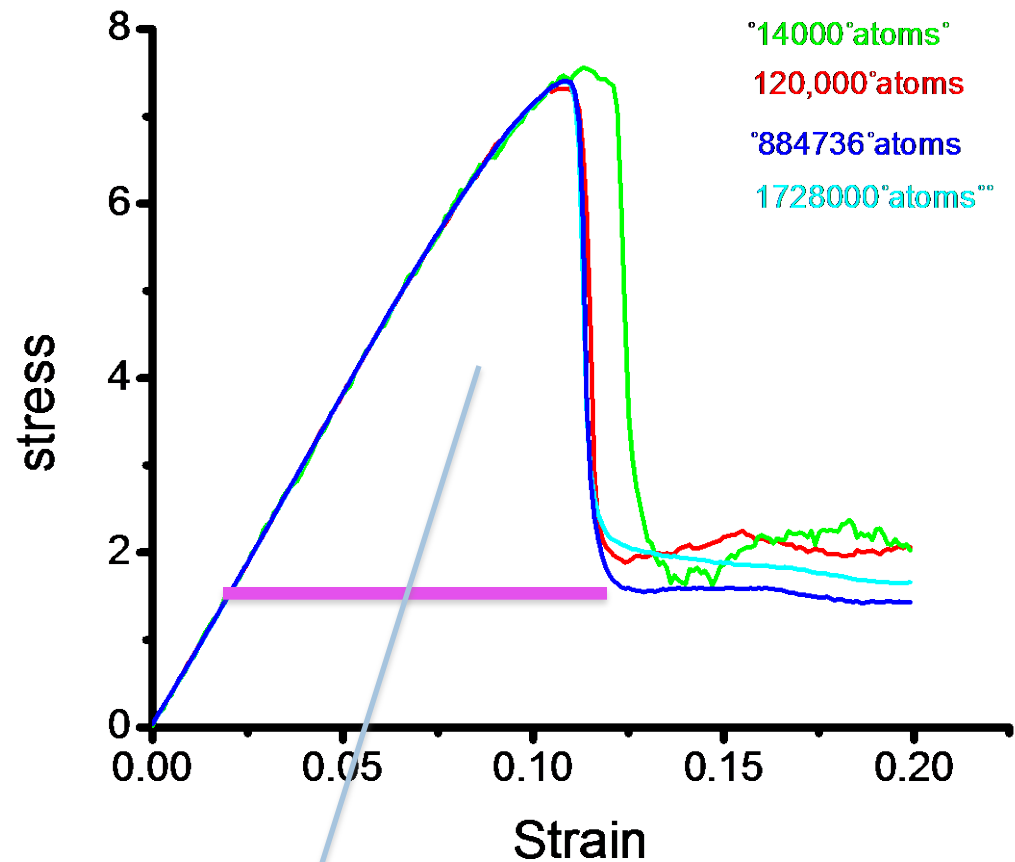
A linear fit gave an average value of Young's Modulus $E = 143$ GPa for bulk LLZO and $E = 121$ GPa for the $\Sigma_3(112)$ grain boundary. (**exp. data 149 GPa**),

Fracture threshold energy



Area under the curve →
Fracture threshold energy
Unit: [J/m²]

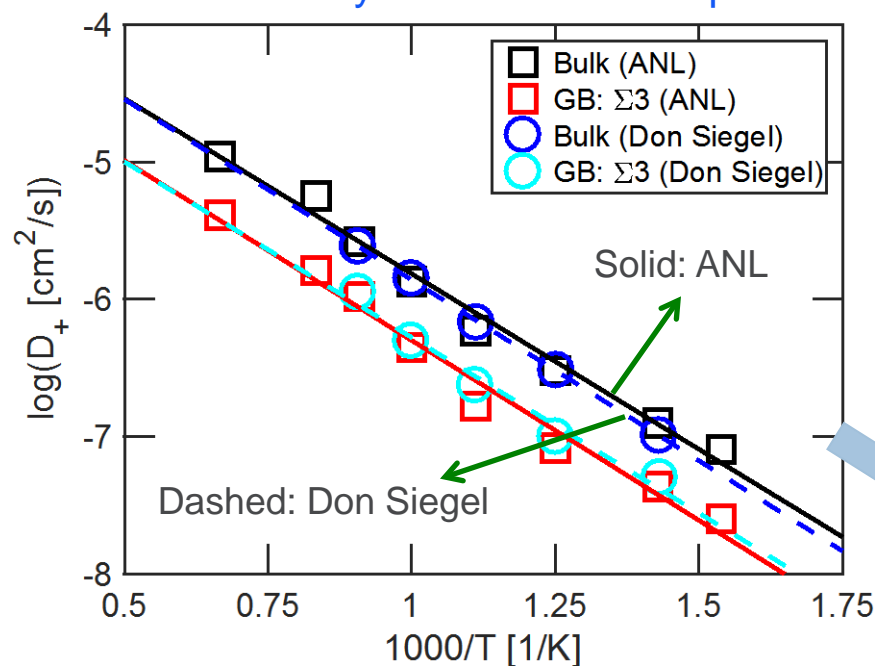
Our simulations for $\Sigma 3(112)$ GBs



5.3 J/m²

Mesoscale analysis: Conductivity of solid state electrolyte

Lithium diffusivity in LLZO w.r.t temperature



Higher concentration of lithium observed within the grain-boundary region.

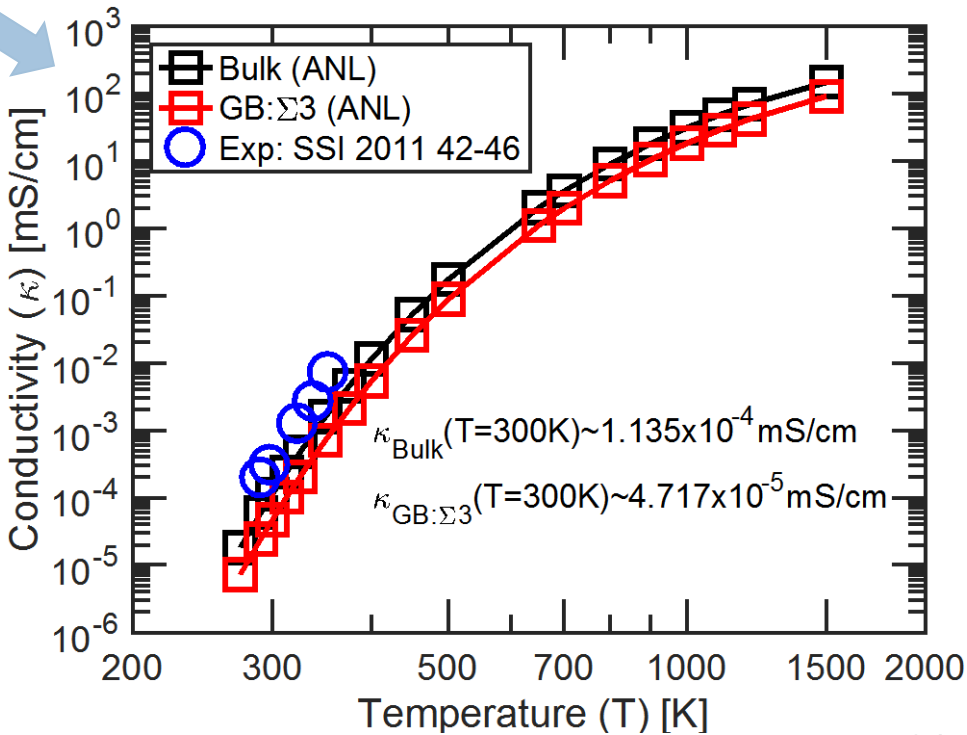
$$c_{+,B} \sim 1.0847 \times 10^{-2} \text{ atoms}/A^{0.3}$$

$$c_{+,GB:\Sigma3} \sim 1.9525 \times 10^{-2} \text{ atoms}/A^{0.3}$$

Lower magnitude of conductivity can be attributed to the absence of dopants within the LLZO lattice structure.

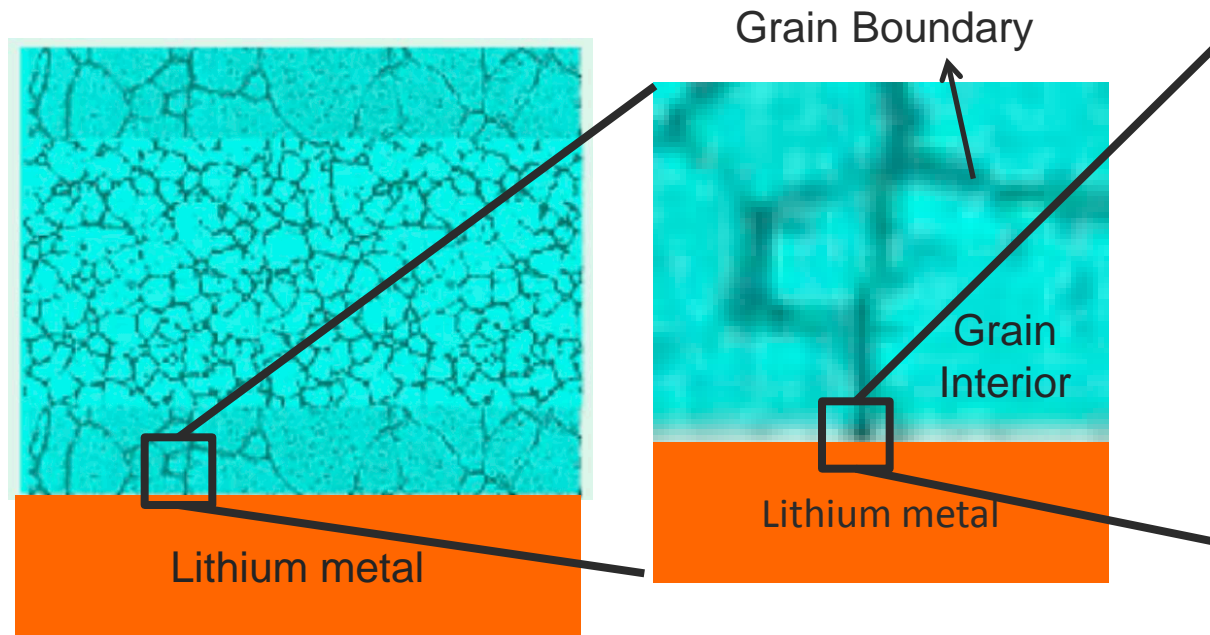
$$\kappa = \frac{F^2 D_+ c_+}{RT}$$

Conductivity in LLZO w.r.t temperature

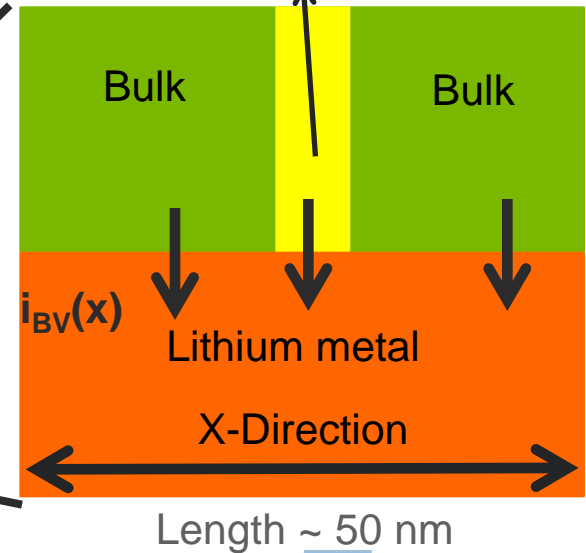


Current focusing at bulk and grain boundary

Schematic of ceramic processes
for fabrication of LLZO SSE



CM calculations
Venkat Srinivasan



(Cheng et al., ACS Appl. Mater. Interfaces 2015, 7, 2073 - 2081)

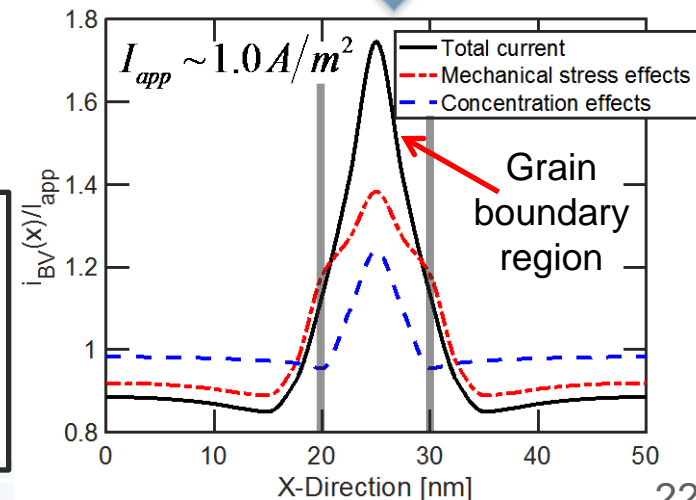
Properties extracted from atomistic calculations:

Young's modulus: $Y_{Bulk} \sim 143 \text{ GPa}$ $Y_{GB:\Sigma 3} \sim 121 \text{ GPa}$

Conductivity: $\kappa_{Bulk} \sim 1.135 \times 10^{-5} \text{ S/m}$ $\frac{\kappa_{GB}}{\kappa_{\sigma}} \sim 0.4155$

Current focusing at grain-boundary because:

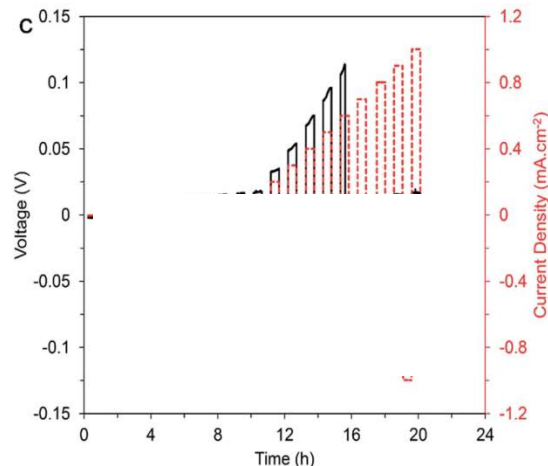
- Higher reference exchange current density
- Lower elastic modulus of the grain-boundary region
- **Similar current focusing at the grain boundaries have been observed by Cheng et al**



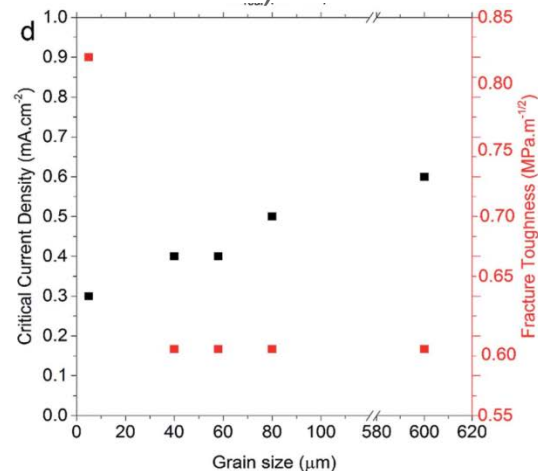


Comparison with experimental results: CM (Venkat Srinivasan's group) with input from atomistic DFT+MD+MC

Experimental Results (Sharafi et al., J. Mater. Chem. A 2017 5 21491 – 21504)

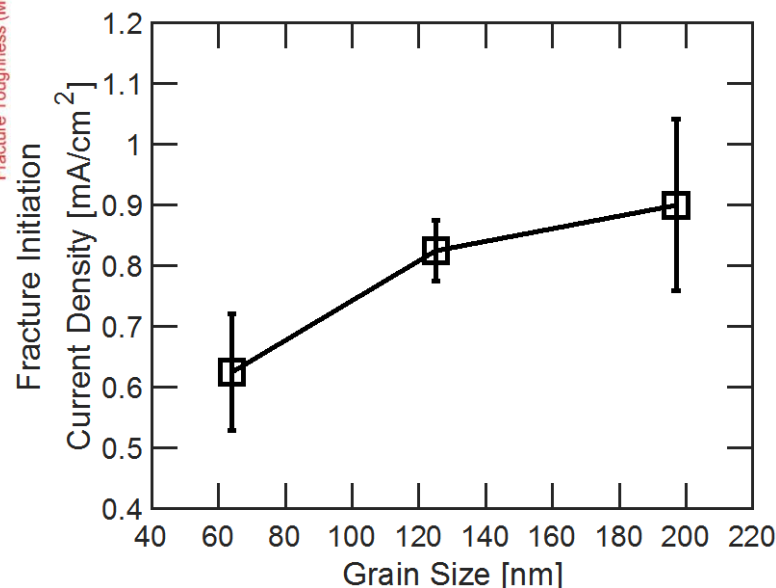


Applied current and voltage response

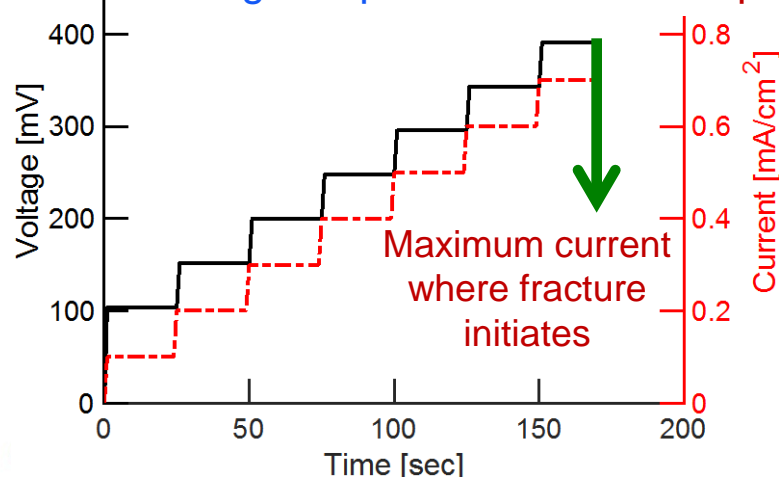


Maximum current density when fracture initiates.

Computationally predicted current density where electrolyte fracture initiates.



Applied current density and corresponding voltage response from the computational model

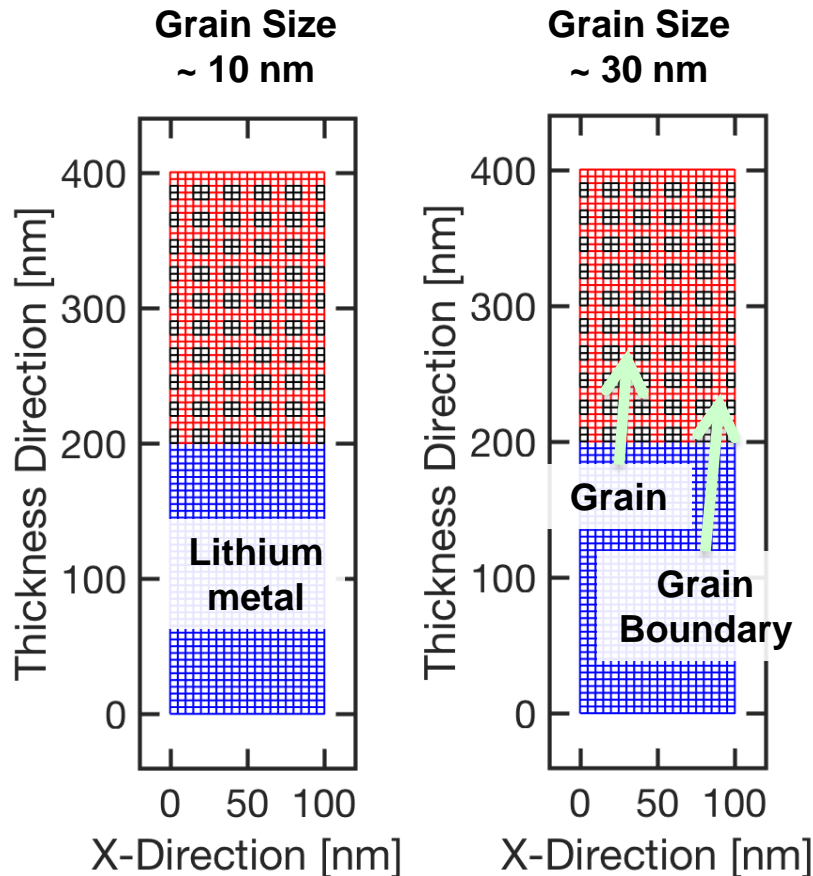


Qualitative comparison with experiments:

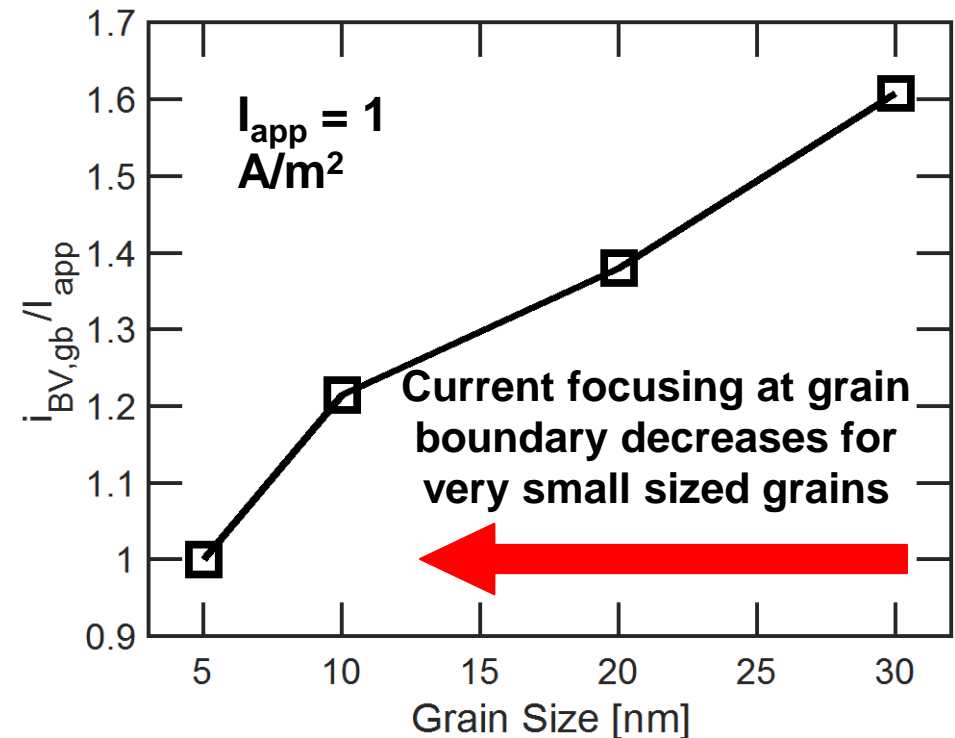
- With increasing grain size, the current density for fracture initiation also increases.
- Current focusing at the grain-boundary is still dominant and governs the overall failure of solid state electrolytes.

How to minimize current focusing at the grain boundary regions

Solid State Electrolyte



Current focusing at the grain boundary with respect to the applied current



Solid state electrolytes with very small grain size, or amorphous materials, may be able to prevent dendrite growth.

Response to last year reviewer's comments

No comments from last year.





Proposed Future Work

- Estimation of lithium transport barrier at the LLZO/NMC interface:
 - Impact of vacancy within NMC and LLZO structure will be studied
 - Effective exchange current density will be estimated at LLZO/NMC interface
 - Interfacial formation/Binding energy between the LLZO and NMC cathode will be calculated
- Estimation of the barrier for Ni, Mn and Co transport between LLZO electrolyte and NMC cathode materials
 - Estimate the propensity of transition metal migration between cathode and solid state electrolyte.
- Incorporate the parameters estimated from atomistic calculations into the continuum level mesoscale model
 - Predict the effect of grain boundary resistance on the overall voltage-capacity performance
 - Estimate the impact of LLZO/NMC delamination and inter-granular fracture on the overall impedance behavior.



Collaborations with other institutions and companies

- V. Srinivasan, P. Barai, ANL
 - Development of continuum based mesoscale models for running simulations using the parameters obtained from atomistic analysis.
- Z. Chen, ANL
 - Experimental characterization of electrode-electrolyte interface
- B. Narayanan, U of Louisville
 - Discussions regarding the atomistic analysis conducted at ANL to estimate elastic and transport properties of LLZO.





Summary

- Atomistic level calculations were used to obtain parameters, DFT, ab initio MD, atomistic MD and MC needed for accurate mesoscale modeling of grain-interior, grain-boundary, and LLZO/Li anode interfaces .
- Interfacial and mechanical degradation mechanisms were investigated at the atomistic level to develop a strategy for minimizing impact on performance
- **The following results were obtained about current focusing that occurs at the grain boundary and can reduces cell performance**
 - Higher current at the grain boundaries leads to enhanced lithium deposition, and formation of dendritic nuclei.
 - Due to the inherent brittleness of the solid electrolytes, these dendritic protrusions can crack the LLZO and propagate through the bulk of the solid electrolyte to the other electrodes and short the cell, which effectively limits its lifetime.
- **Larger grains were studied to determine whether they can help mitigate dendrite growth**
 - Adoption of very large grains leads to minimization of grain boundaries, but dislocations and defects (voids) trapped inside the grains leads to heterogeneity in current distribution, which may lead to current focusing and formation of lithium nuclei.
 - Similarly, the presence of defects in lithium metal may also lead to generation of dendritic protrusions.
 - Hence, best way to prevent dendrite growth may be to approach zero grain size, or amorphous materials.